

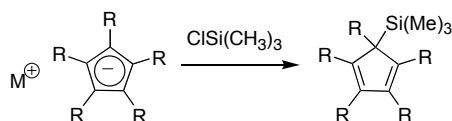
# Niobium Complexes As Lewis Acid and Radical Catalysts

Wayne Tikkanen  
 Department of Chemistry and Biochemistry  
 California State University  
 5151 State University Drive  
 Los Angeles, CA 90032  
 323.343.2372 (vox)  
 323.343.6490 (fax)  
[wayne@calstatela.edu](mailto:wayne@calstatela.edu)

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## Objectives

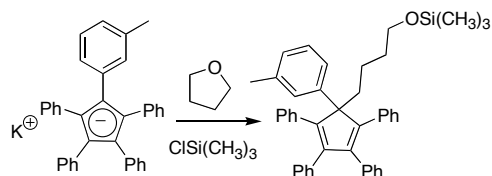
Our goal was to prepare niobium complexes of the pentaphenylcyclopentadienyl ligand, but traditional salt metathesis reactions gave ill characterized products, the pentaphenylcyclopentadienyl radical, or proton abstraction from the solvent. Other groups had successfully used the exchange reaction of trimethylsilylcyclopentadienes with niobium chlorides. We planned to prepare  $C_5Ph_nSiMe_3$  ( $n = 4, 5$ ) by the reaction of a nucleophilic sodium or potassium polyphenylcyclopentadienide with  $SiMe_3Cl$  (Figure 1) for the synthesis of  $C_5H_5SiMe_3$  and  $C_5Me_5SiMe_3$ .<sup>1,7</sup> Rather than using pentaphenylcyclopentadienide, we opted for the more soluble *mt*-yltetraphenylcyclopentadienide (*mt*-Cp) starting material.



Scheme 1. Preparation of TMS-cyclopentadienes (R= H, alkyl)

## Accomplishments to Date

Attempts to prepare trimethylsilyl-*mt*-Cp by the reaction of potassium *mt*-Cp with  $Si(Me)_3Cl$  in a variety of solvents (polar, nonpolar organics and neat TMS-Cl) returned only starting material with the exception of tetrahydrofuran (THF). Removal of solvent in vacuo, followed by addition of (**benzene/toluene**) and filtration gives an off-white solid. The  $^{13}C$  and  $^1H$  NMR spectra as well as HRMS analysis (parent ion = ) indicate that this compound is the result of ring opening of the THF, cleaving the C-O bond giving a product, one isomer of which is shown in Scheme 2.



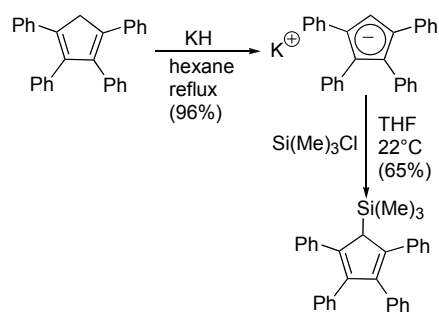
Scheme 2. The Reaction of potassium *mt*-Cp with  $Si(Me)_3Cl$  in THF (=one product isomer shown).

The reason for this unexpected lack of reactivity towards TMS addition may be due to bigger steric hindrance of the five phenyl groups compared to the methyl groups on the pentamethylcyclopentadienyl ring. Ring opening of THF is known to occur through nucleophilic attack when it is coordinated to a Lewis acid.<sup>72</sup> Perhaps the THF ring-opening reaction occurs by THF attacking transient  $SiMe_3-C_5Ph_5$  or THF coordination to  $SiMe_3Cl$  and subsequent attack by the *mt*-Cp anion to give the ring opened product.

<sup>1</sup> Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. J. *Chem. Soc., Dalton Trans.* **1980**, 11556-1160.

<sup>2</sup> ) Gottfried, A. C.; Wang, J.; Wilson, E. E.; Beck, L. W.; Holl, M. M. B.; Kampf, J. W. *Inorg. Chem.* **2004**, 43, 7665-7670.

Suspecting that a less sterically encumbered polyaryl cyclopentadiene would be more amenable



Scheme 3. Synthesis of Tri-methyl-tetraphenylcyclopentadiene

to addition of the TMS group, reaction using a tetra-aryl cyclopentadiene was attempted and  $C_5Ph_4HSiMe_3$  was successfully synthesized. Tetraphenylcyclopentadiene  $C_5Ph_4H_2$  is readily prepared following a reported procedure.<sup>3</sup> The highly air and moisture sensitive potassium tetraphenylcyclopentadienide,  $KC_5Ph_4H$ , is synthesized by reaction of  $C_5Ph_4H_2$  with KH in dried hexane in 96% yield<sup>94</sup> and characterized by  $^1H$  NMR analysis in “superdry”  $CD_3CN$ .<sup>105</sup> Our attempts to make the TMS derivative using diethyl ether, dichloromethane and toluene as solvents gave poor yields. However, reaction of  $KC_5Ph_4H$  with  $SiMe_3Cl$  in anhydrous THF at room temperature gives a tan crystalline solid after crystallization in pentane in 65% yield. In marked contrast to the pentaphenylcyclopentadienyl reaction, no ring opening is observed.  $^1H$  NMR analysis and HRMS analysis confirmed the product as  $C_5Ph_4HSiMe_3$  (Scheme 3).<sup>6</sup>

### Future Work

We are currently pursuing the use of  $C_5Ph_4HSiMe_3$  in the synthesis of niobium complexes and the use of trimethyltincyclopentadienes as a higher yield alternative to the silyl compounds with less potential to go astray in the later metallation steps. At that point we can proceed with investigation of the potential of these complexes as Lewis acid and radical catalysts.

### Publications/Presentations

#646. Diversions and Diversions and Successes in the way to polyphenylcyclopentadienyl niobium(V) complexes, B. Ye, S.C. Osonkie, I. Kriley, G. Tan, A. Chung, W. Tikkanen, 229<sup>th</sup> ACS National Meeting, March 14 (SciMix) and 15<sup>th</sup> 2005, San Diego, CA.

### Students Supported

Stephanie C. Osonkie, M. Monreal, I. Kriley

<sup>3</sup> Castellani, M. P.; Wright, J. M.; Geib, S. J.; Rheingold, A. L.; Troglor, W. C. *Organometallics*, **1986**, 5, 1116-1122.

<sup>4</sup> Equimolar quantities of  $C_5Ph_4H_2$  and KH refluxed in dried hexane 4 hrs, white  $KC_5Ph_4H$  is obtained after filtration.

<sup>5</sup> Deuterated acetonitrile is dried via passage through a 4A° molecular sieves column and stored over 4A° molecular sieves. The  $^1H$  NMR peaks of  $KC_5Ph_4H$  is at CH,  $\delta=6.1$  ppm;  $C_5H_5$ ,  $\delta=6.7-7.2$  ppm.

<sup>6</sup> To a stirred solution of  $KC_5Ph_4H$  in dry THF at room temperature, add  $SiMe_3Cl$  and keep stirring for 0.5 hr. Remove THF and crystallize in pentane. The tan crystalline TMSD is obtained with m.p 123-127°C.  $^1H$  NMR is taken in  $CD_2Cl_2$  with signature pick of  $(CH_3)_3$  at -0.38 ppm and the chemical shift of CH is 4.7 ppm.